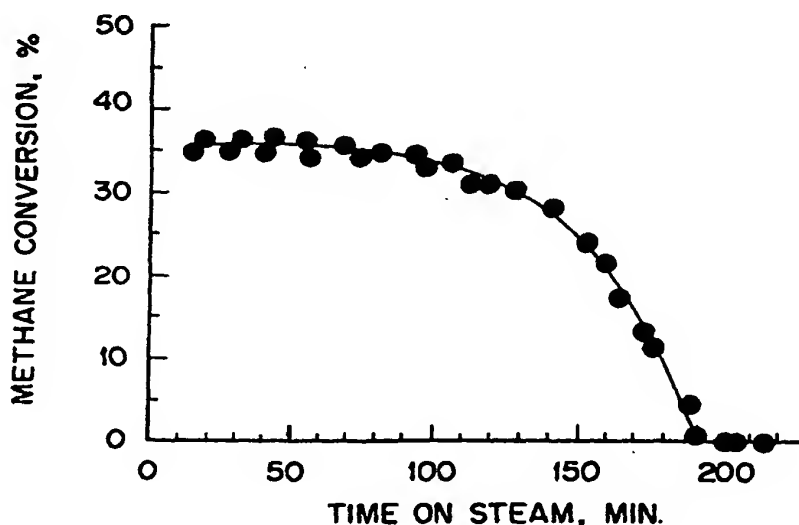




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(54) Title: HYDROGEN PRODUCTION VIA THE DIRECT CRACKING OF HYDROCARBONS



(57) Abstract

A process for producing substantially pure hydrogen by contacting a stream of a hydrocarbon gas with a nickel or nickel-copper containing catalyst at a temperature in the range of about 400 to 900 °C. This results in the conversion of the hydrocarbon gas to substantially pure hydrogen, with said process being carried out until the catalyst is deactivated due to the deposition of carbon on the catalyst. The deactivated catalyst may be regenerated by oxidation in air or by steam gasification of the deposited carbon. The carbon deposited on the catalyst also has separate utility for electrochemical and fuel storage applications and may be recovered for further use.

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Hydrogen Production via the Direct Cracking of Hydrocarbons

Field of the Invention

This invention relates generally to the production of hydrogen, and more specifically to hydrogen production by the direct cracking of hydrocarbons such as methane and natural gas.

5

Background of the Invention

Significant progress made in fuel cell technologies during the past decade has prompted exploration of replacing traditional central large power plants with so-called distributed power generators, consisting of a hydrogen generator and a
10 membrane fuel cell power plant. This latter technology generates electricity at locations where it is aimed to be used, and therefore, eliminates the loss of electricity during its transmission. In addition, a fuel cell process does not emit any environmental pollutants such as NO_x and SO_x which are combustion by-products. Such a process becomes attractive for the automobile industry as well, since vehicles
15 can be propelled by electricity produced from an on-board fuel cell power plant rather than by an internal combustion engine.

The current proton-exchange membrane (PEM) fuel cells utilize hydrogen as the energy source and require essential elimination (ideally below 20 ppmv) of carbon monoxide from the hydrogen stream to prevent poisoning of the
20 electrocatalyst. Hydrogen is typically produced through steam reforming, partial oxidation or autothermal reforming of natural gas. In all these cases, however, carbon monoxide is a co-product, which has to be converted into carbon dioxide in subsequent steps which adds to the cost of the produced hydrogen.

An alternative route is to directly crack the hydrocarbon fuel into hydrogen
25 and carbon. In this case, the formation of carbon oxides is avoided and the need for downstream reactions such as water-gas shift and selective oxidation for the conversion of carbon monoxide to carbon dioxide is eliminated. Surprisingly, this approach has not been extensively studied. While commercial processes exist that utilize thermal cracking of methane at extremely high temperatures for the

production of acetylene and carbon black, hydrogen production via the catalytic cracking of methane has been only briefly considered in the past.

In U.S. Patent 3,361,535 high temperature catalytic cracking of methane is taught. The process taught by the 3,361,535 patent, however, results in the
5 production of undesirable carbon monoxide co-product which requires elaborate additional processing for its conversion to carbon dioxide and results in additional cost.

Recently, Muradov *Int. J. Hydrogen Energy* 18,211(1993), studied the use of iron and nickel oxides supported on alumina as catalysts for the cracking of methane
10 and reported that equilibrium conversions were achieved at temperatures above 800°C. The iron oxide, also appeared to maintain some part of its activity for several hours, in contrast to a Pt/Al₂O₃ catalyst which deactivated within minutes under similar conditions. Muradov *Energy & Fuels* 12,41(1998) has also reported the use of carbon-based catalysts for the same reaction. Although more stable, these
15 catalysts exhibit a lower activity. Furthermore, Ishihara et al. *Shokubai* 35,324(1993); and *Chem. Lett.*, 93(1995); reported that methane cracking takes place at low temperatures over a 10% Ni/SiO₂ catalyst, which does not deactivate even after approximately 200 carbon per nickel atoms have been deposited on it. The results reported by Ishihara, et al., however, did not demonstrate a level of
20 efficiency of hydrogen production which would result in potential commercial use.

Summary of the Invention

It can therefore be seen from the above review of the prior art that an efficient method of directly cracking hydrocarbons to produce hydrogen without the
25 presence of undesirable co-products, such as carbon monoxide, has been an objective in the art.

It is therefore an object of the present invention to provide a method of producing hydrogen by the direct cracking of hydrocarbons.

It is another object of the present invention to provide a method of producing pure hydrogen without carbon monoxide contamination by the direct cracking of hydrocarbons.

It is yet another object of the present invention to produce high purity hydrogen and carbon by the catalytic cracking of hydrocarbons.

5 It is yet a further object of the present invention to provide a method of producing hydrogen by direct cracking of methane through the use of a highly efficient catalyst.

10 It is another object of the present invention to provide a method of producing hydrogen by direct cracking of methane or natural gas at low temperature using a nickel containing catalyst.

It is yet a further object of the present invention to provide a method of producing high purity hydrogen by direct cracking of methane at low temperature using a silica supported nickel-copper catalyst.

15 It has been discovered that the catalytic cracking of methane or natural gas as a potential route for efficient hydrogen production can be accomplished over silica-supported nickel containing catalysts. In one embodiment, activity measurements for the methane cracking reaction were conducted with a 16.4 wt.% Ni/SiO₂ catalyst in a 20% CH₄ in He stream at 550°C and a gas hourly space velocity (GHSV) of 30000 h⁻¹. Under these conditions the catalyst exhibited a high initial activity for the
20 cracking of methane (approximately 35% CH₄ conversion). Hydrogen was the only gaseous product detected. In addition, the rates of methane conversion and hydrogen formation were found to be in ratio of 1:2, thus, verifying the reaction stoichiometry for methane cracking. The amounts of carbon deposited on the spent catalyst and methane reacted indicated a good closure of the carbon balance
25 (100±5%). Upon deactivation of the catalyst due to carbon deposition; catalyst activity may be fully restored by regenerating the catalyst through oxidation in air or steam gasification. The process of the invention may be applicable to any other suitable hydrocarbon such as ethane, ethylene, propane, propylene, butane, pentane, hexane and mixtures thereof, and hydrocarbons with molecular weights in the
30 gasoline and diesel range. Nevertheless, it is anticipated that the preferred

hydrocarbons will be methane and natural gas. During the catalytic cracking of higher molecular weight hydrocarbons, it is expected that several other undesirable products will be formed in addition to the hydrogen.

In a second embodiment, activity measurements for the methane cracking reaction were conducted over a set of 9 Ni-Cu/SiO₂ catalysts in which the total metal amount (on a molar basis) was maintained constant at 2.6 mmole of metal/g of support while the ratio of Ni:Cu was varied from approximately 8:1 to approximately 1:8. The reaction was carried out in a pure methane stream, at 650 and 800 °C and at a gas hourly space velocity of 6000 hr⁻¹. The results indicate that the presence of small amounts of Cu enhanced significantly the Ni activity at 800 °C. The initial conversion over the 2.3 mmole Ni/0.3 mmole Cu/SiO₂ composition for example, was measured at 63%, as compared to 14.4% for the 2.3 mmole Ni/SiO₂ composition. This is a surprising result given that Cu alone is not active for the cracking of methane under these conditions (0.3% initial methane conversion for the 0.3 mmole Cu/SiO₂ composition). The promoting effect is also more pronounced when small amounts of Cu are added (i.e., Ni:Cu ratios greater than 1). The highest initial methane conversion observed with these set of catalysts is at the 8:1 Ni:Cu ratio. Even higher initial methane conversions are expected with higher Ni:Cu ratios up to about 20:1.

20 Brief Description of the Drawings

For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description of a preferred mode of practicing the invention, read in connection with the accompanying drawings, in which:

25 FIG. 1 represents a plot of the deactivation of a Ni/SiO₂ catalyst at 550°C and GHSV = 30,000 h⁻¹ in a stream containing 20% CH₄, in He;

FIG. 2 represents a plot of methane conversions obtained over fresh (●,◆) and regenerated (○ in air, □ in steam) Ni/SiO₂ catalyst at 550°C at two different space velocities;

FIG. 3 represents a plot of selectivities of hydrogen (\diamond at GHSV = 15000 h⁻¹, \blacklozenge at GHSV = 37500 h⁻¹) and carbon dioxide (\circ at GHSV = 15000 h⁻¹, \square at GHSV = 37500 h⁻¹) during steam regeneration of the deactivated Ni/SiO₂ catalyst at 550°C; and

5 Fig. 4 represents a plot of initial methane conversion as a function of catalyst composition at two different temperatures over a series of Ni-Cu/SiO₂ catalysts (\circ at 650 °C and \square at 800°C).

Detailed Description of the Invention

10 The catalyst used in the first embodiment of this invention was prepared by incipient wetness impregnation of an aqueous solution of nickel nitrate onto the silica support, followed by calcination in air and in-situ reduction in flowing hydrogen. This is a standard method of preparation of supported metal catalysts and several different nickel salts can be used instead of nickel nitrate as the nickel
15 precursor. Furthermore, other standard methods for the preparation of supported metal catalysts could be used without having a detrimental effect on the properties of the catalyst. In addition to silica, we investigated other inorganic supports such as alumina and titania. Although nickel supported on these supports was also found to be effective for the catalytic cracking of methane, the performance of nickel
20 supported on silica was superior to those of the other catalysts and therefore, this system was chosen to demonstrate the invention in this application. In addition, we examined the performance of other transition metals such as Co and Fe, supported on silica for this reaction. Although these catalysts were also found to be effective for the reaction, at 550°C the performance of nickel was again superior to the other
25 catalysts. Finally, by examining several Ni/SiO₂ catalysts of variable Ni content, it was determined that optimum performance for the catalytic cracking of methane can be obtained with a nickel content in excess of 5 wt.%, and, in particular a content of approximately 16 wt.%. As a result, a 16 wt.% Ni/SiO₂ catalyst was chosen to demonstrate the invention in this application.

When the catalyst was placed in a conventional fixed bed reactor and exposed to a stream containing 20% CH₄ (by volume) in He, at 550°C and under a GHSV of 30,000 h⁻¹, a high initial activity was observed for the cracking of methane (approximately 35% CH₄ conversion). Hydrogen was the only gaseous product
5 detected and the rates of methane consumption and hydrogen production were found to be in a ratio of 1:2, thus, verifying the reaction stoichiometry for methane cracking.

The catalyst used in the present invention will eventually deactivate as a result of carbon deposition. Carbon may deposit on the surface to cover the active
10 sites (site-blocking) or accumulate at the entrance of the pores to block further access of the reactants to the interior (pore-mouth plugging). It has been estimated that in both cases catalyst deactivation would occur within a short period of time. Even if 10 carbon atoms are needed to block each surface Ni atom, for example, 11 mg of carbon deposition would be enough to completely deactivate one gram of the
15 16.4% Ni/SiO₂ catalyst. Furthermore, if pore-mouth plugging was the main deactivation mechanism, approximately 250 mg of carbon would be sufficient to clog the external 10% of the pores, in one gram of the Ni/SiO₂ catalyst sample.

It has been discovered that a significantly higher amount of carbon deposition on the Ni/SiO₂ catalysts occurs before deactivation occurs. At a
20 temperature of 550°C for example, a very slow deactivation of the Ni/SiO₂ catalyst was observed for the first 2 hours (Figure 1) followed by a more rapid loss of activity during the third hour. By the time the catalyst was completely deactivated (200 minutes), approximately 0.59 g of carbon had accumulated on the 0.2 g of the Ni/SiO₂ catalyst sample. This amount is in very good agreement with the amount of
25 carbon calculated based on the integration of the methane conversion (0.61 g), and corresponds to approximately 2700 carbon atoms accumulated on the catalyst per surface nickel atom.

It is therefore apparent that the capability of the silica supported nickel catalyst to accommodate carbon is significantly higher than those predicted by either
30 the site-blocking or pore-mouth plugging models. Scanning Electron Microscopy

(SEM) and Transmission Electron Microscopy (TEM) analyses of the spent catalysts were utilized to further understand the deactivation mechanism. SEM micrographs indicate the formation of filamentous carbon on the catalyst surface. These filaments appear to grow out of the silica support surface, with their length increasing with time-on-stream. Each filament has a bright tip, identified by the use of SEM/EDS (Energy Dispersive X-Ray Spectroscopy) to be a nickel particle. Spent catalyst samples were further studied by the use of X-Ray Diffraction (XRD). The XRD patterns, suggest that graphitic carbon constituents with different degrees of defect or distortion are present in the deactivated samples. TEM micrographs of the fully deactivated sample show that the growth of the carbon is terminated as a result of spatial limitations. The modes of filament termination include the nickel particle's restriction by the silica surface, the arm and the tip of another carbon filament. Formation of carbon filaments as a result of hydrocarbon cracking has been extensively reported in the literature with higher molecular weight hydrocarbons over supported nickel, iron, cobalt and several alloy catalysts. The carbon deposited on the catalyst in carrying out the present invention may be used in electrochemical applications such as superconductors, electrodes and fuel cells.

The reversibility of filament growth and the regeneration of the catalyst has been previously considered by others, but no results have been reported on whether the catalyst activity can be restored. In fact, some workers have suggested that catalyst regeneration may be futile in view of the changes caused to the catalyst support structure as a result of the filament growth process. Conventional oxidation in air ($C + O_2 = CO_2$) and steam gasification ($C + xH_2O = CO_x + xH_2$) were considered as potential routes for the regeneration of the catalyst at 823 K.

Surprisingly, both methods appear to be able to fully restore the activity of the catalyst, as shown in Figure 2 where the methane conversion is plotted against time-on-stream for the fresh and the regenerated catalysts. The oxidation process was faster than the steam gasification, but caused a high temperature front. This front gradually moved through the catalyst bed, causing the collapse of the sample to a fine powder. XRD analysis suggests that the oxidation process completely removed

the deposited carbon and converted the metallic nickel into nickel oxide which had to be reduced in flowing hydrogen before the next reaction cycle shown in Figure 2. On the contrary, the catalyst bed maintained a uniform temperature profile during the steam regeneration process and the catalyst preserved its metallic nickel form at the end of the process.

Another difference between the two regeneration methods is that the steam gasification leads to the production of additional hydrogen. This is at the expense of external thermal energy, since the oxidation of carbon releases a large amount of heat. Nevertheless, the additional production of hydrogen may be of significant practical importance. Theoretical yields of four and three moles of hydrogen per mole of methane can be achieved respectively, with steam reforming and partial oxidation of methane, provided that all carbon monoxide is converted to carbon dioxide by the water-gas shift reaction. In comparison, methane cracking produces less hydrogen (two moles) from each mole of methane. The hydrogen yield however, can be dramatically improved if the hydrogen produced during the regeneration step is also accounted for. In this case, 2 moles of hydrogen were obtained from each mole of methane during the cracking step and an additional 1.4 moles were produced during the subsequent steam gasification of the deposited carbon, leading to an overall hydrogen yield of 3.4 moles for each mole of methane. This overall hydrogen yield is slightly less than that from steam reforming, but better than that for partial oxidation.

Formation of carbon monoxide and methane were also detected during the initial stage of the steam regeneration, where, as shown in Figure 3, the carbon dioxide and hydrogen selectivities are less than 100%. Increased selectivities of carbon dioxide and hydrogen, obtained when the regeneration was conducted at a higher space velocity, appear to suggest that carbon monoxide and methane may be secondary products, formed due to the reverse water-gas shift ($\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$) and methanation ($\text{CO} + 3 \text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$) reactions. These observations suggest that one may be able to efficiently control the selectivity of hydrogen production during the regeneration step by adjusting the space velocity.

TEM micrographs of the steam regenerated sample show that some remains of the large filaments are still present on this catalyst after the regeneration has been completed. The presence of these remains however, does not appear to have a negative effect on catalytic activity which is fully restored following the steam regeneration step (Figure 2). Following a few cycles of deactivation and steam regeneration however, an air oxidation step will be probably required, to completely remove the accumulated remains.

The set of Ni-Cu/SiO₂ catalysts used in the second embodiment of this invention had the total metal amount (on a molar basis) maintained constant at 2.6 mmole of metal/g of support while the ratio of Ni:Cu was varied from approximately 8:1 to approximately 1:8. The catalysts were prepared by incipient wetness impregnation of nickel and copper nitrates (Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·2.5H₂O) obtained from Aldrich (with a purity of 99.999%) onto commercially available SiO₂ (Davison Syloid 74). Prior to impregnation the silica support was dried, pressed into pellets under a pressure of 15,000 psig, crushed and sieved to obtain a granulometric fraction in the 20-35 mesh size. The impregnated samples were dried in a vacuum oven at 120 °C overnight and subsequently calcined in a muffle furnace at 700 °C for 6 hours. The Ni and Cu loadings were estimated by the weight difference between the blank support and the catalyst reduced overnight in a 1:2 H₂/N₂ mixture (total flow rate of 120 ml/min) at 650 °C.

Following the reduction treatment, the samples were exposed to methane (GHSV - 6000 hr⁻¹) at 650 and 800 °C. Activity measurements were conducted at two different temperatures and the results are presented in Fig. 4. The results indicate that the presence of small amounts of Cu enhanced significantly the initial activity at 800 °C, while the presence of Cu had no significant effect at 650 °C. The initial conversion over the 2.3 mmole Ni/0.3 mmole Cu/SiO₂ composition for example, was measured at 63%, as compared to 14.4% for the 2.3 mmole Ni/SiO₂ composition. This is a surprising result given that Cu alone is not active for the cracking of methane under these conditions (0.3% initial methane conversion for the

-10-

0.3 mmole Cu/SiO₂ composition). The promoting effect is also more pronounced when small amounts of Cu are added (i.e., Ni:Cu ratios greater than 1).

While the present invention has been particularly shown and described with reference to the preferred mode as illustrated in the drawing, it will be understood by one skilled in the art that various changes in detail may be effected therein without departing from the spirit and scope of the invention as defined by the claims.

We Claim:

- 1 1. A process for producing hydrogen which comprises contacting a stream of a
2 hydrocarbon gas with a nickel containing catalyst at a temperature in the range of
3 about 400 to 900°C which results in the conversion of said gas to hydrogen, with
4 said process being carried out until said catalyst is deactivated due to the deposition
5 of carbon on said catalyst.
- 1 2. The process of claim 1 in which the catalyst contains at least 5 wt.% nickel.
- 1 3. The process of claim 1 in which the nickel containing catalyst is supported
2 on an inorganic support.
- 1 4. The process of claim 1 in which the nickel containing catalyst is supported
2 on silica.
- 1 5. The process of claim 1 in which the catalyst further contains copper.
- 1 6. The process of claim 5 in which the ratio of nickel:copper varies from about
2 20:1 to 1:8.
- 1 7. The process of claim 1 in which the hydrocarbon gas is one selected from the
2 group consisting of methane, natural gas, ethane, ethylene, propane, propylene,
3 butane, pentane, hexane and mixtures thereof, and hydrocarbons with molecular
4 weights in the gasoline and diesel range.
- 1 8. The process of claim 1 in which the deactivated catalyst is regenerated by
2 oxidation in air.
- 1 9. The process of claim 1 in which the deactivated catalyst is regenerated by
2 steam gasification of the deposited carbon.

1 10. The process of claim 1 in which the hydrocarbon gas is mixed with an inert
2 carrier gas.

1 11. A process for producing hydrogen which comprises contacting a stream of a
2 hydrocarbon gas with a nickel containing catalyst at a temperature in the range of
3 about 400 to 900°C which results in the conversion of said gas to hydrogen, and
4 where said hydrocarbon gas is one selected from the group consisting of methane
5 and natural gas.

1 12. The process of claim 11 in which the catalyst contains at least 5 wt.% nickel.

1 13. The process of claim 11 in which the nickel containing catalyst is supported
2 on an inorganic support.

1 14. The process of claim 11 in which the nickel containing catalyst is supported
2 on silica.

1 15. The process of claim 11 in which the catalyst further contains copper.

1 16. The process of claim 14 in which the ratio of nickel:copper varies from about
2 20:1 to 1:8.

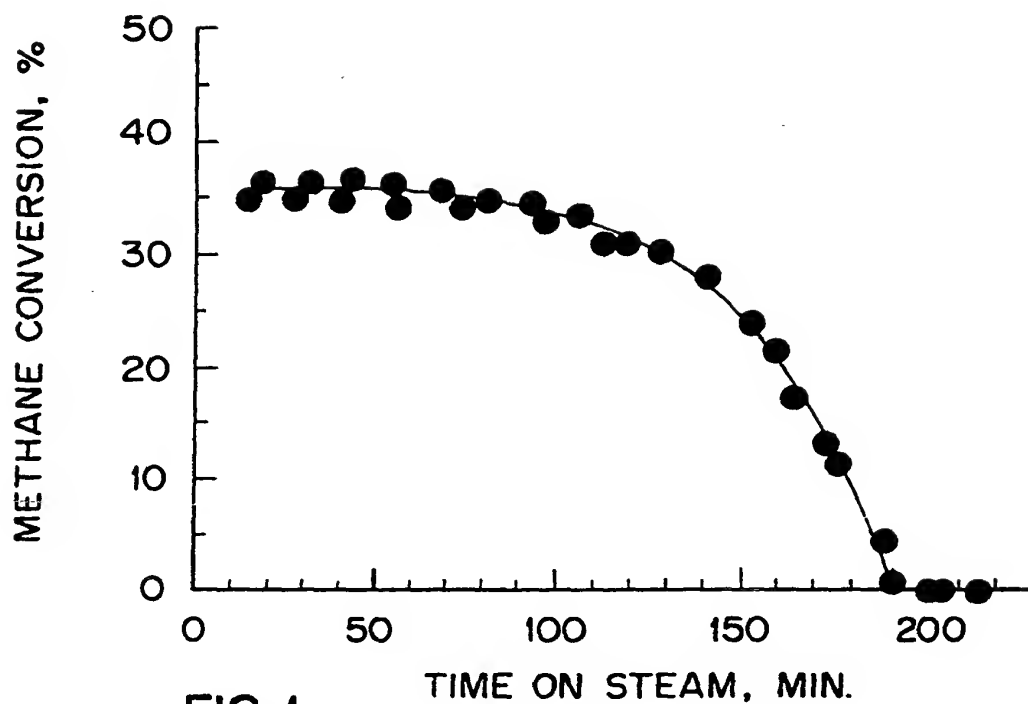
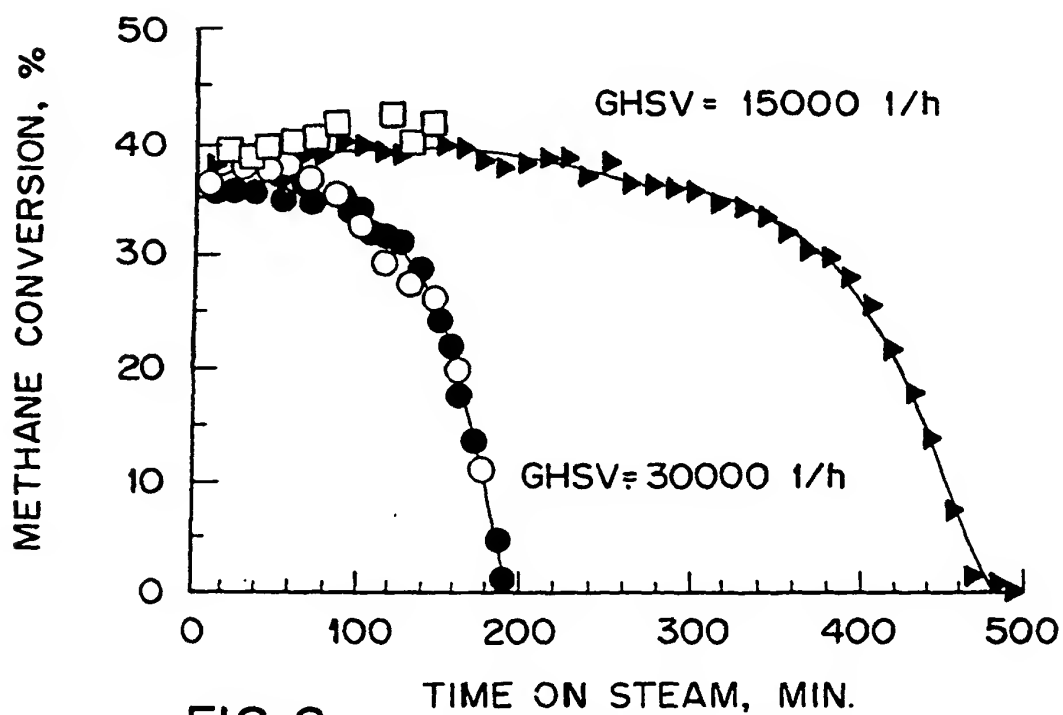
1 17. The process of claim 11 in which the catalyst is regenerated by oxidation in
2 air.

1 18. The process of claim 11 in which the catalyst is regenerated by steam
2 gasification of the deposited carbon.

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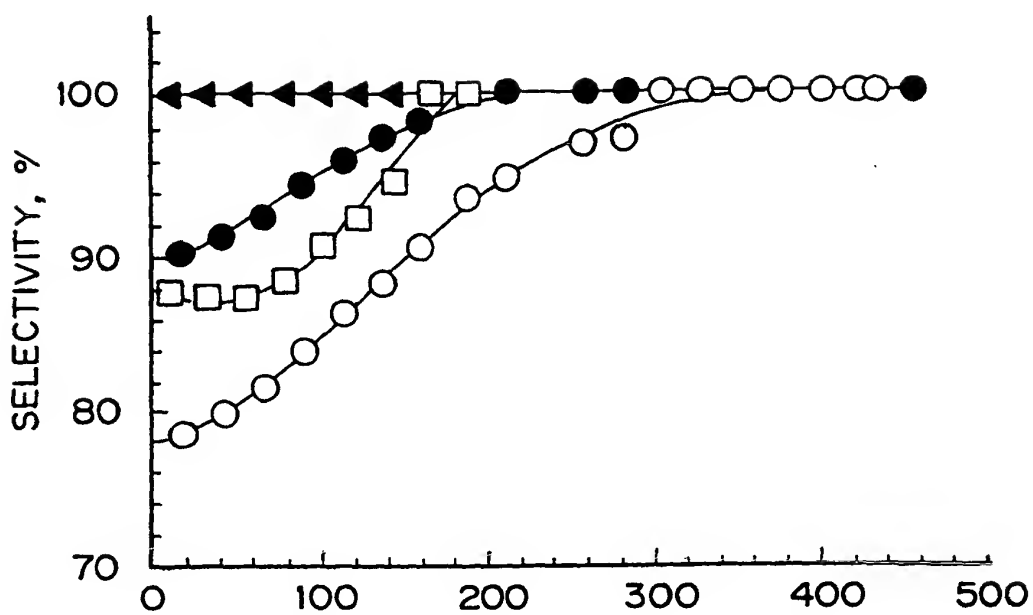
- 1 19. The process of claim 11 in which the hydrocarbon gas is mixed with an inert
- 2 carrier gas.

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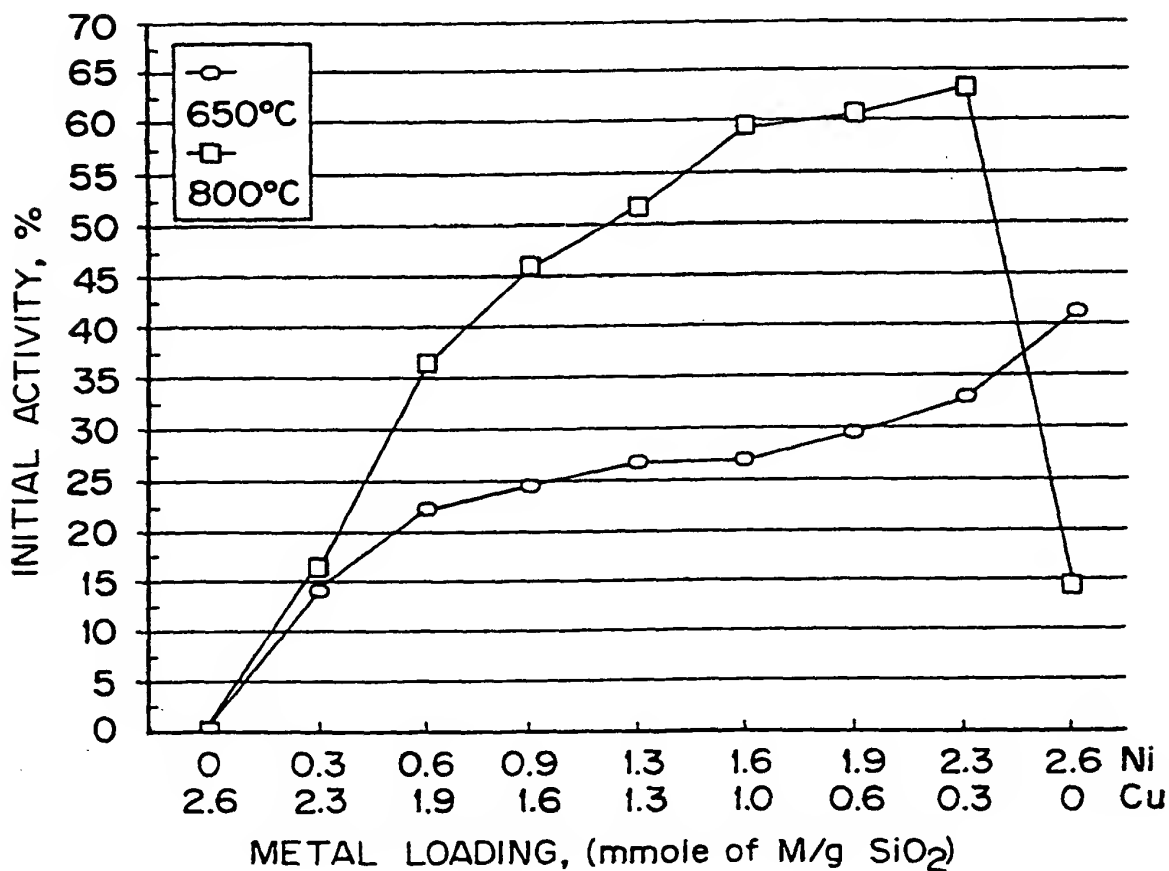
FIG. 1FIG. 2

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**FIG. 3**

TIME ON STEAM, MIN.

**FIG. 4**

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

Inte. .onal Application No

PCT/US 99/03556

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C01B3/26 D01F9/127

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DD 287 015 A (LEIPZIG CHEMIEANLAGEN) 14 February 1991 see the whole document	1-7, 10-16, 19
X	DE 29 46 164 A (STAMICARBON) 3 July 1980 see the whole document	1-4, 7, 10-14, 19
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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10/06/1999

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INTERNATIONAL SEARCH REPORT

Int'l. Application No.

PCT/US 99/03556

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MATSUKATA M ET AL: "Novel hydrogen/syngas production process: Catalytic activity and stability of Ni/SiO ₂ " PROCEEDINGS OF THE 1996 14TH INTERNATIONAL SYMPOSIUM ON CHEMICAL REACTION ENGINEERING. PART B;BRUGGE, BELG MAY 5-8 1996, vol. 51, no. 11 part B, 5 May 1996, pages 2769-2774, XP002103798 Chem Eng Sci;Chemical Engineering Science; Chemical Reaction Engineering: From Fundamentals to Commercial Plants and Products Jun 1996 Pergamon Press Inc, Tarrytown, NY, USA see the whole document	1-4,7, 10-14,19
X	Abstracts of Papers, part 2 211th ACS National Meeting, March 24-28, 1996: T. Zhang "Deactivation and regeneration of silica-supported nickel catalysts during methane cracking" XP002104030 see abstract	1-4,7,9, 11-14,18
X	US 4 435 376 A (PORTER RANDALL A ET AL) 6 March 1984 see the whole document	1-3,7, 10-13,19
X	FENELONOV V B ET AL: "Structure and texture of filamentous carbons produced by methane decomposition on Ni and Ni-Cu catalysts" CARBON, vol. 35, no. 8, 1 January 1997, page 1129-1140 XP004086485 see page 1129 - page 1130 see page 1138	1-7, 10-16,19
X	PATENT ABSTRACTS OF JAPAN vol. 098, no. 005, 30 April 1998 & JP 10 007928 A (TOYOTA MOTOR CORP), 13 January 1998 see abstract	1-4,7, 10-14,19

INTERNATIONAL SEARCH REPORT

Information on patent family members

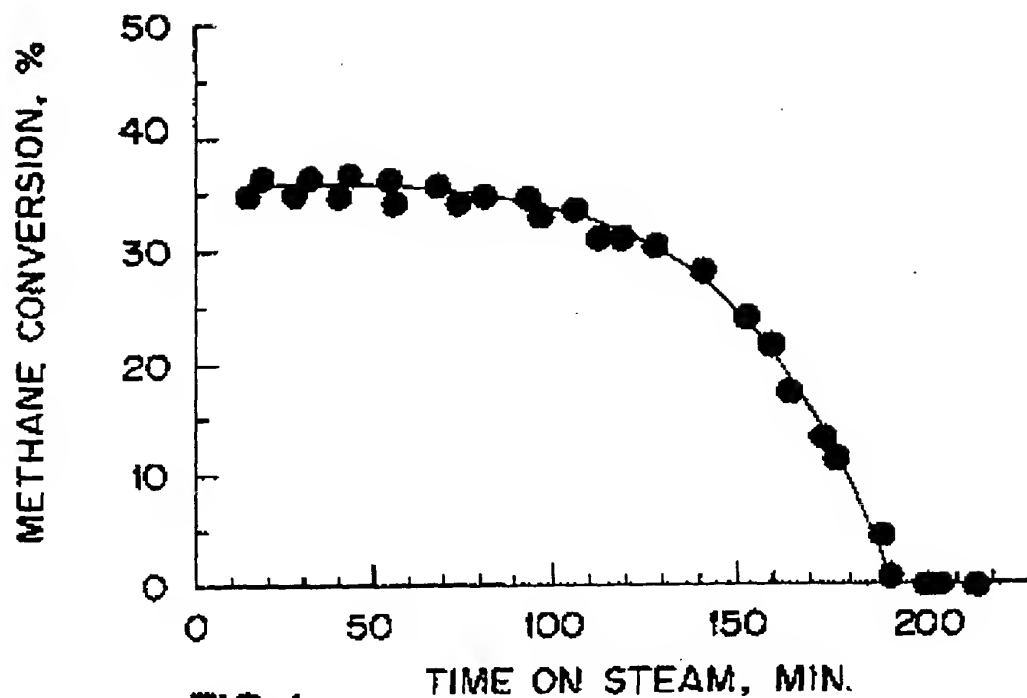
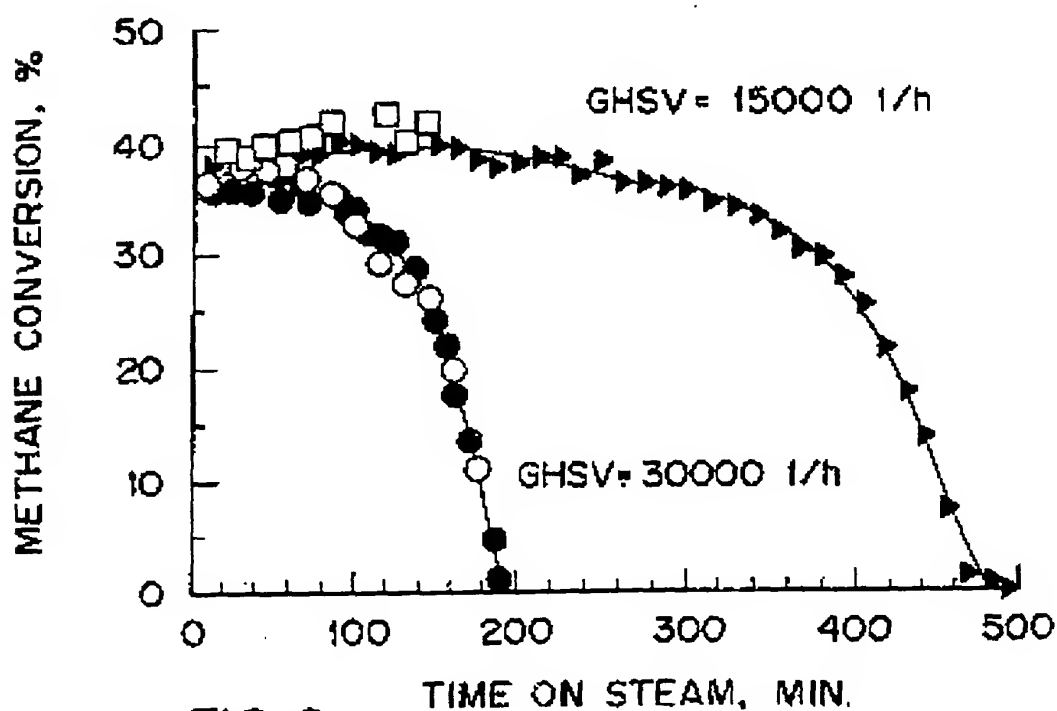
International Application No

PCT/US 99/03556

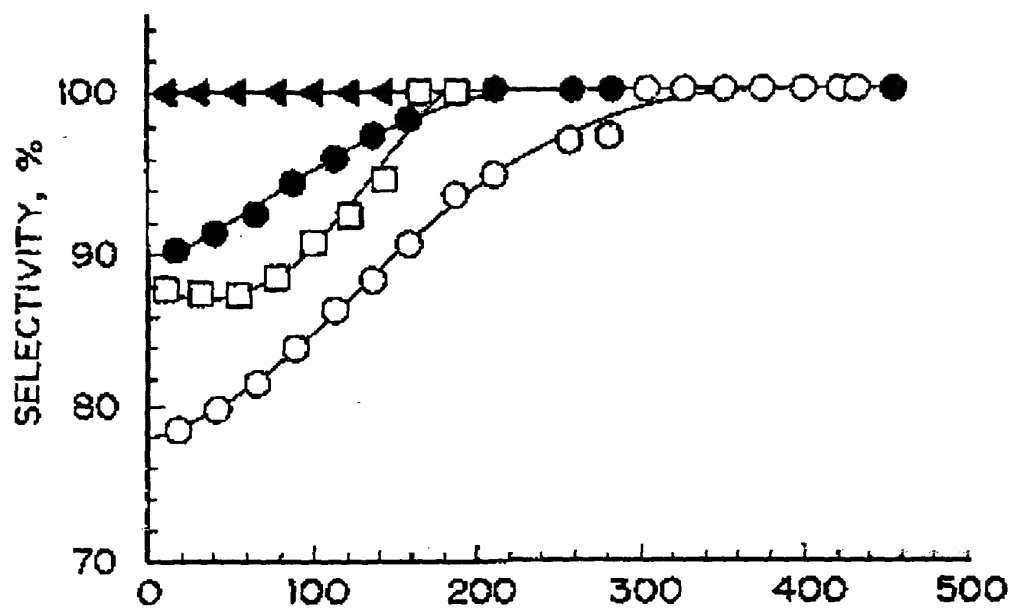
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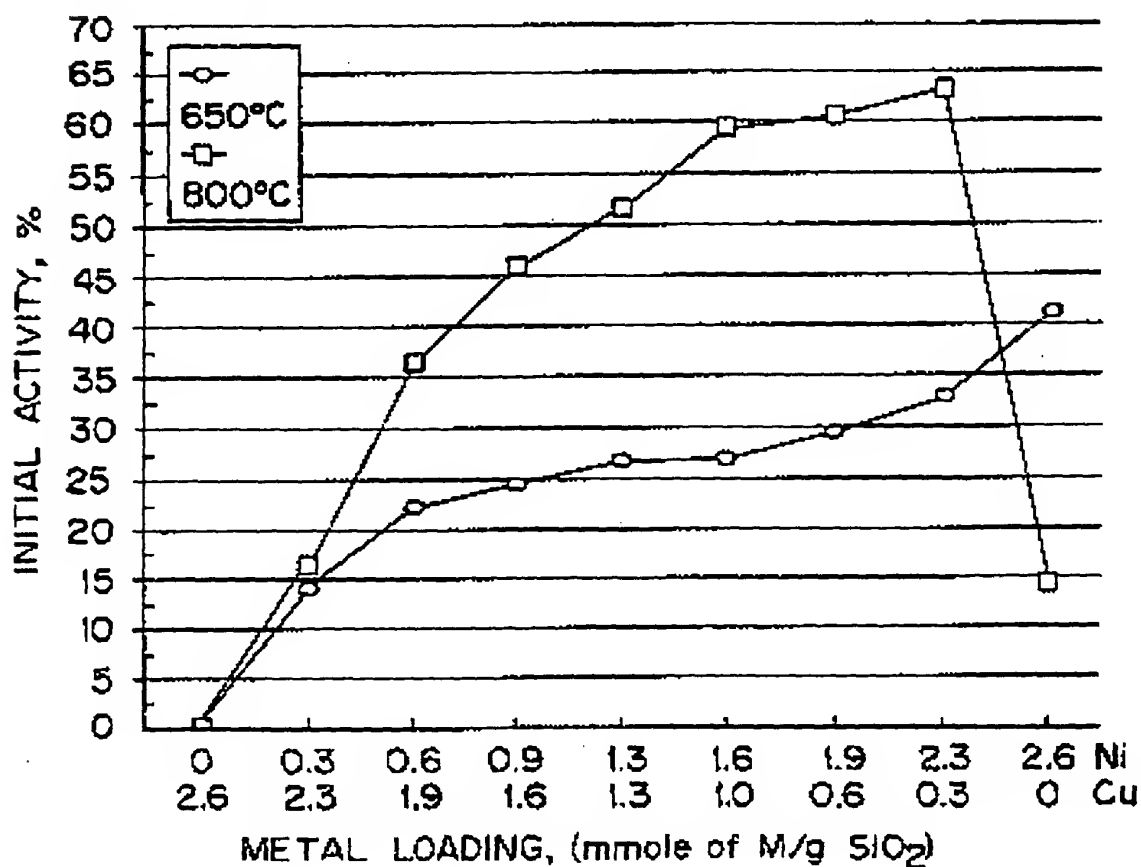
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FIG. 1FIG. 2

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**FIG. 3**

TIME ON STEAM, MIN.

**FIG. 4**

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